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Project Summary

Determination of Volatile Organics in Industrial and Municipal Wastewaters

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This program was undertaken in an effort to develop analytical methodologies for the determination of volatile organics in industrial and municipal wastewaters. The efforts were directed exclusively toward analytical techniques employing gas chromatography with flame ionization and halogen-specific detectors.

A number of gas chromatographic column packings were evaluated in an effort to find a set of optimum operating conditions. Direct aqueous injection, solvent extraction, and purge and trap techniques were evaluated as means of sample introduction. The most satisfactory results were obtained using the Bellar-Lichtenberg purge and trap method with both FID and Coulson detectors.

Stability of the test compounds as solutions in methanol and n-butanol was evaluated after 30-, 60-, and 90-day periods. Preservation of aqueous samples containing residual chlorine for a one week period was studied; aliquots of reducing agents, added to the sample before storage, were found to aid in maintaining chemical stability.

The methods developed were tested on spiked industrial wastewater samples in order to evaluate their applicability to real world situations. The methods were found to be satisfactory for relatively "clean" samples. For grossly contaminated samples, however, the methods suffer from interferences caused by lack of detector specificity.

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This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Under provisions of the Clean Water Act, the United States Environmental Protection Agency (EPA) is required to promulgate guidelines establishing test procedures for the analysis of pollutants. The Clean Water Act Amendments of 1977 emphasize the control of toxic pollutants and declare the 65 "priority" pollutants and classes of pollutants to be toxic under Section 307(a) of the Act. This report is one of a series that investigates the analytical behavior of selected priority pollutants and suggests a suitable test procedure for their measurement.

The purpose of the current study was to develop and evaluate various techniques for analysis of volatile organics by gas chromatography. Thirty-six compounds were studied. While this study developed analytical methods

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specifically for these compounds, they could apply to analysis of other compounds as well. A list of the compounds studied is found in Table 1.

As part of this study, several gas chromatographic column packing materials were evaluated with respect to their ability to separate as many of the compounds as possible. Detection was accomplished by means of flame ionization, electron capture, and Coulson electrolytic conductivity detectors. Direct aqueous injection, liquid/liquid extraction, and purge and trap techniques were studied as methods of sample introduction. The effects of storage conditions upon the chemical stability of aqueous samples containing trace levels of test compounds and residual chlorine were studied. An effort was made to determine a set of optimum conditions for water sample storage.

The methods developed were applied to the analysis of industrial wastewaters. Samples from five industrial categories were analyzed by direct injection using FID and Coulson detectors, by liquid extraction using the electron capture detector, and by purge and trap using FID and Coulson detectors. The results of the various analyses were compared for each of the industrial samples.

Table 1. *Retention Times of Test Compounds*

Compound	Retention times (min.) Column 1	Column 2	Column 3
1 dichlorodifluoromethane	1.7	0.95	1.3
2 methyl chloride	0.7	0.54	1.8
3 vinyl chloride	—	1.0	1.6
4 methylbromide	1.4	0.8	2.2
5 chloroethane	2.5	1.3	2.5
6 trichlorofluoromethane	6.3	2.3	5.0
7 1,1-dichloroethylene	6.9	3.6	3.4
8 methylene chloride	4.1	4.5	3.6
9 1,2-trans-dichloroethylene	8.8	5.2	4.7
10 acrolein	4.7	4.2	2.5
11 1,1-dichloroethane	8.2	4.5	5.6
12 chloroform	9.3	6.7	5.9
13 1,1,1-trichloroethane	10.9	8.8	9.2
14 carbon tetrachloride	11.3	9.3	8.2
15 acrylonitrile	5.4	4.8	3.2
16 benzene	14.0	13.8	8.8
17 1,2-dichloroethane	10.0	7.5	8.2
18 trichloroethylene	13.6	12.7	9.9
19 dichlorobromomethane	11.8	10.5	10.2
20 2,3-dichloropropene	12.9	11.5	10.0
21 1,2-dichloropropane	12.9	11.6	10.3
22 dibromomethane	10.1	10.0	10.4
23 1,3-trans-dichloropropylene	13.1	12.1	10.8
24 2-chloroethylvinyl ether	15.0	14.0	10.7
25 toluene	19.1	23.3	11.7
26 1,3-cis-dichloropropene	14.2	13.5	11.0
27 1,1,2-trichloroethane	14.2	13.6	11.3
28 chlorodibromomethane	14.0	13.6	12.6
29 1-chlorocyclohexene	18.7	—	14.3
30 tetrachloroethylene	18.1	18.3	13.4
31 1,2-dibromoethane	14.9	14.4	12.7
32 chlorobenzene	20.0	20.4	13.0
33 ethylbenzene	21.8	26.7	13.7
34 1,1,2,2-tetrachloroethane	18.0	18.6	14.5
35 bromoform	16.2	16.3	14.1
36 p-dichlorobenzene	27.3	—	17.2

Column 1: 1.8 m x 2 mm glass with 1% SP1000 on Carbopack B, 60-80 mesh; Program-Inject at 50°C; hold 5 min, then up 10°c/min to 225°C for 5 min

Column 2: 1.8 m x 2 mm glass with 0.2% Carbowax 1500 on Carbopack C, 60-80 mesh; Program Inject at 40°C; hold 4 min, up 10°C/min to 175°C, hold 10 min.

Column 3: 4 m x 2 mm i.d. glass with 20% SP2100/0.1% Carbowax 1500 on 100-125 mesh Supelcoport; Program-Inject at 50°C; hold 4 min, up 10°C/min to 170°C, hold 4 min.

Development of Analytical Methods

Chromatography

Three approaches for analyzing wastewater for thirty-six volatile organic compounds were evaluated: the purge and trap technique, the direct aqueous injection approach, and the solvent extraction approach. The first two approaches employed both the flame ionization detector (FID) and the Coulson electrolytic conductivity detector. The third approach utilized the electron capture detector (ECD). Except as subsequently specified, all the chromatographic column packing materials tested were compatible with any of the analytical approaches.

No gas chromatographic column was found which could separate all the test compounds in a single programmed run. Tenax GC, 3% SP-2510, and Chromosorb 102 were tried and found to be unsatisfactory for general use. These columns were rejected primarily because of inadequate separation of a number of compounds, or, in some cases, because of poor chromatography. For a specific subset of the purgeables, however, these column materials may be suitable in a given wastewater.

Three columns which did show adequate separation of most compounds, in addition to good chromatography (sharp peaks, no tailing), were 1% SP-1000 on Carbopack B (60-80 mesh), 0.2% Carbowax 1500 on Carbopack C (60-80 mesh), and 20% SP-2100/0.1% Carbowax 1500 on Supelcoport (100-120 mesh). The retention times of each compound on these columns along with the column dimensions and temperature programs are given in Table 1. A close examination will show that those compounds which do not separate on the 1% SP-1000 column, for example, will separate on the 20% SP-2100, and vice versa. Thus, by comparing retention times on two columns, sufficient separation of all compounds can be achieved.

Purge and Trap

The purge and trap technique was evaluated with respect to its ability to detect 1 ppb of all the test compounds. A key factor is the purgeability of the test compounds from aqueous solution. The recovery of test compounds from water

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was determined by comparing the detector response from a purge and trap analysis to that from a direct injection of the same mass of a given compound into the same chromatographic system. Except where noted, the following purge and trap conditions were employed:

Purge time:	10-15 minutes
Purge Temperature:	ambient (22-25°)
Desorb Time:	5 minutes
Desorb Flow Rate:	25 mL/minute
Desorb Temperature:	200°C
Sample Size:	5 mL

The purging efficiencies of all the test compounds were measured using the approach described above. Measurements were made at 10 ppb. Results for two traps are shown in Table 2. The data shows that, in some cases, recoveries determined using the Tenax/Carbosieve B (HT) trap (Trap 2) are greater than those determined using the Tenax/silica trap (Trap 1).

Particularly noteworthy are the results for acrolein and acrylonitrile. The Trap 2 recoveries equal those obtained with Trap 1 even after increasing purging temperature and ionic strength. The results suggest that polymerization or irreversible absorption are the cause of low recovery, and not poor purging efficiency.

Compounds having a lower boiling point than trichlorofluoromethane were not trapped effectively by the Tenax/silica trap. Therefore, various Tenax/charcoal traps were prepared and tested for their ability to trap these gaseous compounds. Data were obtained for Tenax/Carbosieve B (HP) traps and for Tenax/SKC charcoal traps. For each trap, purge times of 10 and 15 minutes were tested.

Based upon the results, a number of conclusions can be drawn: 1) Charcoal/Tenax traps are effective adsorbants for the compounds tested; 2) five to seven cm of charcoal are required for a retentive trap; 3) recoveries of some compounds are lower using the longer 15 minute purge times. This indicates that gaseous compounds are easily desorbed from these traps at room temperature.

Table 2. *Purge and Trap Efficiencies of Test Compounds*

Compound	*Purge and Trap Efficiency[a] Trap 1[b]*	*Trap 2[c]*
trichlorofluoromethane	*78*	*85*
1,1-dichloroethylene	*82*	*120*
methylene chloride	*82*	*140*
1,2-trans-dichloroethylene	*104*	*92*
1,1-dichloroethane	*100*	*95*
chloroform	*76*	*83*
1,1,1-trichloroethane	*86*	*108*
carbon tetrachloride	*60*	*87*
trichloroethylene	*77*	*71*
1,2-dichloroethane	*74*	*100*
dichlorobromomethane	*85*	*134*
1,2-dichloropropane	*83*	*88*
1,3-trans-dichloropropylene	*87*	*72*
1,3-cis-dichloropropylene	*58*	*60*
1,1,2-trichloroethane	*89*	*85*
chlorodibromomethane	*72*	*91*
tetrachloroethylene	*82*	*48*
chlorobenzene	*110*	*81*
1,1,2,2-tetrachloroethane	*28*	*82*
bromoform	*49*	*77*
dibromomethane	*93*	*81*
2-chloroethylvinyl ether	*21*	*45*
1,2-dibromoethane	*56*	*60*
2,3-dichloropropene	*87*	*93*
1-chlorocyclohexene	*68*	*105*
p-dichlorobenzene	*100*	*120*
benzene	*41*	*82*
toluene	*38*	*123*
ethylbenzene	*28*	*48*
acrolein	*9*	*44*
acrylonitrile	*15*	*41*

[a] *Determined by comparing the response by purge and trap to that obtained by direct injection of the test compound.*

[b] *Tenax/silica trap obtained from Tekmar, Inc. Purge time 15 min.*

[c] *Tenax/Carbosieve B(HT) (Supelco, Inc., Bellefonte, Pa) trap prepared in our laboratory, 14 cm Tenax + 7 cm Carbosieve B (HT). Purge time 15 min.*

Solvent Extraction/Electron Capture Detection

The purposes of this aspect of the study were to determine the optimum conditions of extraction using a simple extraction procedure, the accuracy and precision of the extraction process at the one ppb level; and the suitability of the extraction solvents n-pentane and isooctane.

The first extraction techniques tested were those in which no head space was allowed in the extraction vessel. Various methods of agitation were tested and the pentane layer analyzed by electron capture gas chromatography. The extraction efficiency for each compound was determined by comparison with standards of known concentration. It quickly became apparent that very vigorous agitation methods are needed to get efficient extractions when there are no headspace bubbles to help mix the two phases.

If, on the other hand, one allows a small amount of headspace, very good extraction efficiencies can be obtained by simple hand shaking for only one minute. Trichlorofluoromethane and compounds boiling above trichlorofluoromethane could be extracted with high efficiency.

The variation in response of the electron capture detector to the test compounds is quite pronounced. For those compounds containing three or more halogens, the response is sufficiently high that one can readily detect 1 ppb or less. The monohalogenated compounds and even the dichloroethanes and dichloropropanes cause such a poor response that 100 ppb would be difficult to detect at the same detector setting used for the trihalogenated compounds. Typical estimated detection limits and extraction efficiencies for the more sensitive compounds are presented in Table 3. For the

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Table 3. *Method Detection Limit and Extraction Efficiencies for Polyhalogenated Compounds*

Compound	MDL[a] (ppb)	Extraction Efficiency
dichlorodifluoromethane	1	NA
trichlorofluoromethane	0.8	NA
chloroform	0.3	88
1,1,1-trichloroethane	0.02	100
carbon tetrachloride	0.02	100
trichloroethylene	0.04	97
chlorodibromomethane	0.1	100
dibromomethane	0.1	65
1,1,2-trichloroethane	0.3	91
chlorodibromomethane	0.1	100
tetrachloroethylene	0.02	100
1,1,2,2-tetrachloroethane	0.04	100
bromoform	0.04	100

[a]*MDL=minimum detection limit; calculated as follows:*

$$MDL = \frac{(Area)}{\frac{(Response\ area\ units)}{gm}(35\ mL)(5\ uL)} \frac{(2\ mL)}{} \frac{in\ gm}{uL}$$

remaining compounds, the sensitivity of the detector is relatively poor.

The MDLs for Table 3 were calculated using a minimum area of 200 units. The response was determined from the regression analysis of each curve. Further assumptions were 35 mL sample extracted with 2 mL pentane and an injection volume of 5 microliters.

The solvents tested were pentane and isooctane. Both were shown to be satisfactory. However, even Nanograde Quality batches from three different suppliers contained low boiling, electron capture responsive contaminants. These could not be eliminated by distillation. Furthermore, elution of the solvent normally caused a negative peak, which would interfere with quantitation of any compound eluting at the same time.

Direct Aqueous Injection

Direct injection of aqueous solution of the test compounds was studied using the FID and Coulson detectors to evaluate the utility of the method in detecting the compounds at ppm levels. Using the same chromatographic columns as used for the other methods, it has been demonstrated that one ppm of almost every compound can be detected. The exceptions were methyl chloride (10 ppm) and p-dichlorobenzene (2 ppm). Columns may require an injection of blank water prior to analysis until a clean blank run is obtained, because water seems to clean the column of strongly absorbing compounds. The 20% SP-2100 column is particularly good for aqueous injection. The 0.2% carbowax 1500 column, however, does not work well for aqueous injections. The water appears to uncover active sites which bind some compounds irreversibly and thus show a progressive loss of sensitivity during repeated runs.

Preservation Study

The aim of the preservation study was to determine the effects of certain storage parameters on the integrity or chemical stability of clean water samples containing trace levels of the test compounds at the ppb level. Parameters investigated were temperature (4°C and 25°C), pH (2, 7 and 10), and the presence of reducing agents (ascorbate, thiosulfate, and sulfite) added to destroy any residual chlorine. Samples were prepared and stored for seven days under various sets of conditions and analyzed by purge and trap to determine recovery of each of the compounds.

1,1,2,2-tetrachloroethane is not preserved at pH 10 under any conditions. Loss of 2-chloroethylvinyl ether occurs at pH 2 and 7. Formation of trace quantities of unidentified compounds was observed in many of the unpreserved chlorinated samples. These results alone indicate the value of adding a reducing agent when collecting chlorine treated wastewater effluents for volatile organic analyses. The value of adding a reducing reagent may be even greater for actual wastewater samples which may contain many non-volatile organics, since it is well established that chlorine reacts with compounds such as humic acids to produce trihalomethanes.

Application Phase

The methods described in preceding sections were tested on industrial and municipal wastewater effluents. Analysis of actual wastewater samples allows one to evaluate the effect of the presence of non-volatile organics and other dissolved solids which are typically present in wastewater. One can also evaluate the flexibility of each method in handling wide variations in concentration and number of compounds.

Selection and Preparation of Industrial Samples

The industrial categories used in this study were selected to give a range of difficulty in analysis. The five industries selected were:

1. Organic Chemicals Industry (Industrial Category #12)
2. Publicly Owned Treatment Works (POTW)
3. Auto and Other Laundries (Industrial Category #19)
4. Coal Mining Industry (Industrial Category #11)
5. Pulp and Paper Industry (Industrial Category #16)

Previous work with samples from these industries indicated that their effluents contained a wide range of volatiles concentration. In each of the above industries, a number of samples were available in California Analytical Laboratory. Several samples in each industry were composited to yield two liters of wastewater from each industry. These samples were representative of the industry and are not typical of a single plant or treatment facility. Thus, these composited samples may represent a "worst case" for each industry.

Each composited industrial sample was analyzed five ways: 1) direct aqueous injection using the FID; 2) direct aqueous injection using the Coulson detector; 3) liquid/liquid extraction with the electron capture detector; 4) purge and trap with the Coulson detector; and 5) purge and trap with the FID. All the GLC data collected in the application phase were obtained using a 4mx2mm(id) glass column packed with 20% SP-2100/0.1% carbowax 1500 on 100-120 mesh supelcoport.

After the initial analyses, the samples were spiked with the test compounds at 20 ppb and divided into two portions.

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One portion was analyzed immediately by purge and trap. The second portion was placed in a septum sealed 40 mL vial and placed in the refrigerator to be analyzed one week later.

Analysis of Composited Samples

Direct Aqueous Injections

The results of direct aqueous injection, for the POTW sample, using both the FID and the Coulson detectors are given in Table 4. Peaks in the samples which matched a standard retention time within 0.1 minute were listed as positive identifications. The only other criterion used was the selectivity of the Coulson detector. For the halogenated compounds, if a peak appearing in the FID run was not confirmed by the Coulson run, then the peak was ignored. Furthermore, for those halogenated compounds having a high FID response, both detectors had to see a peak before a quantitation was reported. Since the Coulson detector is highly selective for halogenated compounds, all peaks found by that detector which correspond to the retention time of one of the test compounds are indicated in the tables, but only those peaks which are confirmed by the FID analysis are quantitated.

Table 4. *Results of Analysis of Publicly Owned Treatment Works Composited Sample*

Compound	Retention Time (min)	Direct Inject FID	Direct Inject Coulson	Solvent Extraction EC	Purge and Trap FID	Purge and Trap Coulson
dichlorodifluoromethane	1.3					
vinyl chloride	1.6					
methyl chloride	1.8					
methyl bromide	2.2					
chloroethane	2.5	60				
acrolein	2.5					
acrylonitrile	3.2					
1,1-dichloroethylene	3.4					
methylene chloride	3.6					
1,2-trans-dichloroethylene	4.7					*
trichlorofluoromethane	5.0					
1,1-dichloroethane	5.6					
chloroform	5.9			5		9
carbon tetrachloride	8.2			0.4		
1,2-dichloroethane	8.2					
benzene	8.8	300				
1,1,1-trichloroethane	9.2					
trichloroethane	9.9			2		
2,3-dichloropropene	10.0				0.5	2
dichlorobromomethane	10.2					
1,2-dichloropropane	10.3					
dibromomethane	10.4					
2-chloroethylvinyl ether	10.7					
1,3-dichloroproylene	10.8					
1,3-cis-dichloropropylene	11.0					
1,1,2-trichloroethane	11.3					
toluene	11.7					
chlorodibromomethane	12.6					
1,2-dibromoethane	12.7					
chlorobenzene	13.0					
tetrachloroethylene	13.4			11	11	9
ethylbenzene	13.7					
bromoform	14.1					
1-chlorocyclohexene	14.3					
1,1,2,2-tetrachloroethane	14.5					
p-dichlorobenzene	17.2					

All results are given in parts per billion (ppb).
**Peak detected; not quantitated.*

It should be noted that two industrial category samples, organic chemicals and auto and other laundries, yielded a large number of peaks by FID analysis, but only a small number by Coulson analysis. This made identification difficult in some cases. In any event, it seems certain that there are a number of volatile compounds present in these effluents, at the ppm level, which are not compounds under study here.

Analysis by Solvent Extraction and Electron Capture Detection

The results of this analysis are found in column five of Table 4. As expected, this method is capable of detecting levels of some compounds not seen by the purge and trap method. However, there are a few instances where compounds are reported at a level which should have been seen by the other methods but they were not. In general, the agreement between the extraction method and purge and trap is good.

Analysis by Purge and Trap

Columns six and seven of Table 4 contain the results of the purge and trap analyses. The same criteria for quantitation was used as in the direct injection analysis. The quantitative agreement between the two detectors is poor, but using the selectivity of the Coulson as a guide and an examination of the chromatograms indicate the FID is responding to other compounds that are present in the sample. In almost every case, the FID is measuring higher values than the Coulson, which is consistent with the above hypothesis.

Analysis of Spiked Samples

As described previously, each of the industrial composites were spiked with 20 ppb of each of the test compounds. The spiked solutions were transferred to six 40 mL glass screw capped vials and sealed with Teflon lined silicon rubber septums. Three of these vials were immediately analyzed by purge and trap, while three were stored in a refrigerator for one week, then analyzed. The results for the POTW sample are seen in Table 5. The concentration shown for the spiked compounds are the average of three determinations ± the relative standard deviation.

The gases dichlorodifluoromethane, methyl chloride, methyl bromide and chloroethane were not seen, probably due to a very rapid loss from the working solution. In order to see these com-

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Table 5. *Analysis of Publicly Owned Treatment Works Spiked Sample*

Compound	Spike level (ppb)	Concentration Determined (ppb) Background	Spiked Day 0	Spiked Day 7
dichlorodifluoromethane	30.7			
methyl chloride	26.9			
methyl bromide	33.1			
chloroethane	28.0			
acrolein*	33.6		20±58%	18±67%
acrylonitrile*	17.0		6±16%	109±59%
1,1-dichloroethylene	23.8		40±16%	16±48%
methylene chloride	21.2		70±7%	83±41%
1,2-trans-dichloroethylene	21.4		31±13%	11±111%
trichlorofluoromethane	14.9		Masked	Masked
1,1-dichloroethane	20.8		21±11%	38±3%
chloroform	24.0	9	35±2%	30±5%
carbon tetrachloride	17.9		21±4%	11±3%
1,2-dichloroethane	20.2		33±7%	15±29%
benzene*	22.0		36±38%	20±39%
1,1,1-trichloroethane	22.6		25±19%	10±34%
trichloroethylene	23.0		21±1%	16±14%
2,3-dichloropropene	20.0		20±17%	12±9%
dichlorobromomethane	21.4	2	22±3%	45±3%
1,2-dichloropropane	22.4		20±17%	12±9%
dibromomethane	20.0		29±1%	14±14%
2-chloroethylvinyl ether*	20.0		13±24%	13±7%
1,3-trans-dichloroproplyene	11.9		12±4%	19±29%
1,3cis-dichloropropylene	11.9		10±8%	16±44%
1,1,2-trichloroethane	25.0		28±3%	27±1%
toluene*	22.8	0.5	19±101%	11±7%
chlorodibromomethane	26.6		30±2%	13±9%
1,2-dibromoethane	23.6		19±7%	49±2%
chlorobenzene*	21.4		11±22%	5±6%
tetrachloroethylene	20.8	9	36±4%	15±1%
ethyl benzene	19.9		1±16%	0.2±0%
bromoform	19.9		20±12%	71±20%
1-chlorocyclohexene*	20.0		12±18%	11±6%
1,1,2,2-tetrachloroethane	20.8		24±0%	20±27%
p-dichlorobenzene*	20.6		17±16%	16±2%

**These compounds were analyzed using the FID. All others were analyzed using Coulson Detector.*

pounds, an alternative spiking procedure must be used. However, their rapid loss strongly suggests that they are not likely to be found in an industrial effluent unless sampling is done very soon after the gases enter the effluent.

In general, the precision of analysis was poor. One significant factor was the frequent presence of interfering compounds and the occasional high levels of some test compounds in the sample prior to spiking. These situations caused sufficient skewing or distortion of the chromatograms such that correct integration of peaks was not accomplished. It was usually not possible to check peak heights against integrator values, but in the few instances where it was possible, the precision was usually within 10% relative standard deviation. A second factor was the carryover between replicate runs. High levels of some compounds made carryover a significant problem. Due to time constraints, blanks were not run between replicates, but only between different samples.

Conclusions and Recommendations

Methodologies for the analysis of volatile organic compounds in industrial and municipal wastewater have been developed and evaluated, using gas chromatography with the flame ionization, electron capture, and Coulson detectors. Several improvements in existing analytical methods have been realized. Some of the current techniques require further development.

Although no single GC column was found that gives complete chromatographic separation of all the test compounds, several GC packing materials were identified that provide good chromatographic separation of all but a few of the test compounds.

All the test compounds were detected by one or more of the analytical approaches studied at levels of 1 ppb or less. The nonhalogenated compounds are not detected by Coulson or electron capture. Many of the compounds are detectable at levels of 0.1 ppb or lower.

The stability of the test compounds as standards in organic and as "clean" samples in aqueous media was studied in detail. The addition of preservatives to reduce residual chlorine in aqueous samples was found to help maintain the integrity (chemical stability) of aqueous samples containing residual chlorine and trace quantities of the test compounds.

The major limitation of all the analytical approaches investigated in this study was the lack of specificity of detection. The FID was the only detector of those studied that was able to detect the nonhalogenated compounds. However, it was the least specific of the detectors studied. For relatively "clean" wastewaters, a combination of the analytical methods developed on this project have been found to usually be both specific and sensitive. However, for grossly polluted wastewaters, interferences became such a severe problem that qualitative identification was not feasible.

Further study is recommended to develop either sample cleanup procedures for use prior to analysis, or to find an analytical scheme more specific to the test compounds of interest before these or similar methods can become generally applicable for analysis of complex industrial or municipal wastewaters. Other areas recommended for further study include: further evaluation of the precision and accuracy of the methods developed herein, evaluation of alternative trap materials to be used in the purge and trap approach, and development of alternative methods for the analysis of acrolein and acrylonitrile.

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The complete report, entitled "Determination of Volatile Organics in Industrial and Municipal Wastewaters," (Order No. PB 82-119 090; Cost: $10.50, subject to change) will be available only from:
National Technical Information Service
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